

CLAIMS

1. A polyimide block copolymer composition for use as a film, photosensitive polyimide, film insulating varnish,
5 photoresist, electroplating polyimide, printing varnish, sealant or adhesive, comprising:

(a) a four-component or higher polyimide block copolymer containing pyromellitic dianhydride, obtained by reacting an oligomer terminated with diamines at both ends,
10 which is a reaction product of pyromellitic dianhydride (1 mole) and diaminotoluene (1.5-2 moles) , with an acid dianhydride other than pyromellitic dianhydride and an aromatic diamine, wherein the molar ratio between the molar ratio of the total aromatic diamines to the total acid
15 dianhydrides is 1-0.95; and

(b) a polar solvent containing a hydrocarbon.

2. A polyimide block copolymer composition for use as a film, photosensitive polyimide, film insulating varnish, photoresist, electroplating polyimide, printing varnish,
20 sealant or adhesive, comprising:

(a) a four-component or higher polyimide block copolymer containing pyromellitic dianhydride, obtained by reacting an oligomer terminated with acid dianhydrides at both ends, which is a reaction product of an acid
25 dianhydride other than pyromellitic dianhydride (2 moles) and an aromatic diamine (1-1.5 moles) , with pyromellitic dianhydride and an aromatic diamine, wherein the molar ratio of the aromatic diamine to pyromellitic dianhydride

is 1.5-2 and the molar ratio of the total aromatic diamines to the total acid dianhydrides is 1-0.95; and

(b) a polar solvent containing a hydrocarbon.

3. A polycondensation product composition containing
5 pyromellitic dianhydride and having benzoxazole groups and imide groups for use as a film, photosensitive polyimide, film insulating varnish, photoresist, electroplating polyimide, printing varnish, sealant or adhesive, comprising:

10 (a) a four-component or higher polycondensation product containing pyromellitic dianhydride and having benzoxazole groups and imide groups, obtained by reacting an oligomer terminated with diamines at both ends, which is a reaction product of pyromellitic dianhydride (1 mole) and
15 diaminotoluene (1.5-2 moles) , with an acid dianhydride other than pyromellitic dianhydride and an aromatic diamine having a hydroxyl group and an amino group in the ortho positions, wherein the molar ratio of the total aromatic diamines to the total acid dianhydrides is 1-0.95; and

20 (b) a polar solvent containing a hydrocarbon.

4. A four-component or higher polycondensation product composition containing pyromellitic dianhydride and having benzoxazole groups and imide groups for use as a film, photosensitive polyimide, film insulating varnish,
25 photoresist, electroplating polyimide, printing varnish, sealant or adhesive, comprising:

(a) a four-component or higher polycondensation product containing pyromellitic dianhydride and having

benzoxazole groups and imide groups, obtained by reacting an oligomer terminated with acid dianhydrides at both ends, which is a reaction product of an acid dianhydride other than pyromellitic dianhydride (2 moles) and an aromatic
5 diamine having a hydroxyl group and an amino group in the ortho positions (1-1.5 moles) , with pyromellitic dianhydride and an aromatic diamine having a hydroxyl group and an amino group in the ortho positions, wherein the molar ratio of the aromatic diamine to pyromellitic
10 dianhydride is 1.5-2 and the molar ratio of the total aromatic diamines to the total acid dianhydrides is 1-0.95; and

(b) a polar solvent containing a hydrocarbon.

5. A process for preparing a four-component or higher
15 polyimide block copolymer solution containing pyromellitic dianhydride, comprising:

(a) a first step of reacting pyromellitic dianhydride (1 mole) and diaminotoluene (1.5-2 moles) in a polar solvent containing a hydrocarbon at 160-200 °C in the
20 presence of an acid catalyst to give an oligomer terminated with diamines at both ends; and

(b) a second step of adding an acid dianhydride other than pyromellitic dianhydride and an aromatic diamine to the reaction product and heating the mixture at 160-200 °C
25 to react it, wherein the molar ratio of the total aromatic diamines to the total acid dianhydrides is 1-0.95.

6. The process for preparing a polyimide block copolymer solution of claim 5, wherein a member selected from the

group consisting of 3,3'-diaminodiphenyl sulfone, 1,3-bis (3-aminophenoxyphenyl)benzene, bis[4-(3-aminophenoxy)phenyl]sulfone, 9,9-bis (4-aminophenyl)fluorene, 3,5-diaminobenzoic acid, 3,4'-

5 diaminodiphenyl ether, bis(3-amino-4-hydroxyphenyl)sulfone, and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane is used in place of the diaminotoluene.

7. A process for preparing a four-component or higher polyimide block copolymer solution containing pyromellitic
10 dianhydride, comprising:

 (a) a first step of reacting an acid dianhydride other than pyromellitic dianhydride (2 moles) and an aromatic diamine (1-1.5 moles) in a polar solvent containing a hydrocarbon at 160-200 °C in the presence of
15 an acid catalyst to give an oligomer terminated with acid dianhydrides at both ends; and

 (b) a second step of adding pyromellitic dianhydride and an aromatic diamine to the reaction product and heating the mixture at 160-200 °C, wherein the molar ratio of the
20 aromatic diamine to pyromellitic dianhydride is 1.5-2 and the molar ratio of the total aromatic diamines to the total aromatic tetracarboxylic acid dianhydrides is 1-0.95.

8. The process of claim 5 or 7 wherein the hydrocarbon is selected from the group consisting of toluene, xylene
25 and mixtures thereof; the polar solvent is selected from the group consisting of N-methylpyrrolidine, N,N-dimethylacetamide, N,N-dimethylformamide, N-methylformamide, tetramethylurea, dimethyl sulfoxide, sulfolane and mixtures

thereof; and the amount of the polyimide block copolymer to be dissolved in the polar solvent containing a hydrocarbon is 10% by weight or more, preferably 15-25% by weight.

9. The process of claim 5 or 7 wherein the acid catalyst
5 is a binary catalyst consisting of γ -valerolactone and pyridine or methyldmorpholine.

10. The process of claim 5 wherein the acid dianhydride other than pyromellitic dianhydride is 3,4,3',4'-biphenyltetracarboxylic dianhydride, 3,4,3',4'-
10 benzophenonetetracarboxylic dianhydride, 2,2-bis (3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, 3,4-dicarboxyphenyl sulfone anhydride, bis (3,4-dicarboxyphenyl) ether anhydride, or 2,3,6,7-naphthalenetetracarboxylic anhydride.

15 11. A process for preparing a four-component or higher polycondensation product containing pyromellitic dianhydride and having benzoxazole groups and imide groups, comprising:

(a) a first step of reacting pyromellitic dianhydride
20 (1 mole) and diaminotoluene (1.5-2 moles) in a polar solvent containing a hydrocarbon at 160-200°C in the presence of an acid catalyst to give an oligomer terminated with diamines at both ends; and

(b) a second step of adding an acid dianhydride other
25 than pyromellitic dianhydride and an aromatic diamine having a hydroxyl group and an amino group in the ortho position to the reaction product and heating the mixture at 160-200°C to react it, wherein the molar ratio of the total

aromatic diamines to the total acid dianhydrides is 1-0.95.

12. A process for preparing a four-component or higher polycondensation product containing pyromellitic dianhydride and having benzoxazole groups and imide groups, comprising:

(a) a first step of reacting an acid dianhydride other than pyromellitic dianhydride (2 moles) and an aromatic diamine having a hydroxyl group and an amino group in the ortho positions (1-1.5 moles) in a polar solvent containing a hydrocarbon at 160-200 °C in the presence of an acid catalyst to give an oligomer terminated with acid dianhydrides at both ends; and

(b) a second step of adding pyromellitic dianhydride and an aromatic diamine to the reaction product and heating the mixture at 160-200°C, wherein the molar ratio of the aromatic diamine having a hydroxyl group and an amino group in the ortho positions to pyromellitic dianhydride is 1.5-2 and the molar ratio of the total aromatic diamines to the total aromatic tetracarboxylic acid dianhydrides is 1-0.95.

13. The process of claim 11 or 12 wherein the aromatic diamine having a hydroxyl group and an amino group in the ortho positions is selected from the group consisting of 3,3'-dihydroxybenzidine, 3,3'-dihydroxy-4,4'-diaminodiphenyl ether, 1,4-bis (3-hydroxy-4-aminophenyl)benzene, 2,2-bis (3-amino-4-hydroxyphenyl)propane, bis (3-amino-4-hydroxyphenyl)sulfone, 2,4-diaminophenol, 2,5-diaminophenol, and 2,2-bis[4- (3-amino-4-hydroxyphenyl)]hexafluoropropane.

14. A polyimide block copolymer composition for use as a film, photosensitive polyimide, insulating varnish, electroplating polyimide, printing varnish, sealant or adhesive, comprising:

5 (a) a four-component or higher polyimide block copolymer obtained by reacting an oligomer terminated with diamines at both ends, which is a reaction product of pyromellitic dianhydride (1 mole) and diaminotoluene (1.5-2 moles) , with benzophenonetetracarboxylic dianhydride and
10 an aromatic diamine, wherein the molar ratio of the total aromatic diamines to the total acid dianhydrides is 1.00-0.95; and

(b) a polar solvent containing a hydrocarbon.

15. A polyimide block copolymer composition for use as a
15 film, photosensitive polyimide, insulating varnish, electroplating polyimide, printing varnish, sealant or adhesive, comprising:

(a) a four-component or higher polyimide block copolymer obtained by reacting an oligomer terminated with
20 acid dianhydrides at both ends, which is a reaction product of benzophenonetetracarboxylic dianhydride (2 moles) and diaminotoluene (1-1.5 moles) , with pyromellitic dianhydride and an aromatic diamine, wherein the molar ratio of the aromatic diamine to pyromellitic dianhydride
25 is 1.5-2 and the molar ratio of the total aromatic diamines to the total acid dianhydrides is 1.00-0.95; and

(b) a polar solvent containing a hydrocarbon.

16. A process for preparing a four-component or higher

polyimide block copolymer solution, comprising:

(a) a first step of reacting pyromellitic dianhydride (1 mole) and diaminotoluene (1.5-2 moles) in a polar solvent containing a hydrocarbon at 160-200°C in the presence of an acid catalyst to give an oligomer terminated with diamines at both ends; and

(b) a second step of adding benzophenonetetracarboxylic dianhydride and an aromatic diamine to the reaction product and heating the mixture at 160-200°C to react it, wherein the molar ratio of the total aromatic diamines to the total acid dianhydrides is 1.00-0.95.

17. A process for preparing a four-component or higher polyimide block copolymer solution, comprising:

(a) a first step of reacting benzophenonetetracarboxylic dianhydride (2 moles) and diaminotoluene (1-1.5 moles) in a polar solvent containing a hydrocarbon at 160-200°C in the presence of an acid catalyst to give an oligomer terminated with acid dianhydrides at both ends; and

(b) a second step of adding pyromellitic dianhydride and an aromatic diamine and heating the mixture at 160-200°C to react it, wherein the molar ratio of the aromatic diamine to pyromellitic dianhydride is 1.5-2 and the molar ratio of the total aromatic diamines to the total tetracarboxylic dianhydrides is 1.0-0.95.

18. The process of claim 16 wherein a member selected from the group consisting of bis[4-(3-

aminophenoxy)phenyl]sulfone, bis[4-(4-aminophenoxy)phenyl]sulfone, 1,3-bis (3-aminophenoxy)benzene, 9,9-bis (4-aminophenoxy)fluorene, 3,5-diaminobenzoic acid, 3,4'-diaminodiphenyl ether,
5 2,2-bis[3-amino-4-phenoxyphenyl] hexafluoropropane and bis(3-amino-4-phenoxyphenyl)sulfone is used in place of the diaminotoluene.

19. The process of claim 17 wherein a member selected from the group consisting of 4,4'-diaminodiphenyl sulfide,
10 2,2-bis [4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, bis[4- (3-aminophenoxy)phenyl]sulfone, bis[4- (4-aminophenoxy)phenyl]sulfone, 1,3-bis (3-aminophenoxy)benzene, 9,9-bis (4-aminophenoxy)fluorene,
15 3,5-diaminobenzoic acid, 3,4'-diaminodiphenyl ether, 2,2-bis[3-amino-4-phenoxyphenyl] hexafluoropropane and bis(3-amino-4-phenoxyphenyl)sulfone is used in place of the diaminotoluene.

20. The process of claim 16 wherein the acid catalyst is
20 a binary catalyst consisting of (a) γ -valerolactone and (b) pyridine and/or N-methylmorpholine.

21. The process of claim 16 or 17 wherein the hydrocarbon is toluene and/or xylene; and the polar solvent is a liquid containing one or two members selected from the group
25 consisting of N-methylpyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, tetramethylurea and sulfolane.

22. The process of claim 21 wherein the polyimide block

copolymer is 10% by weight or more, preferably 15-25% by weight based on the total weight of the solution.

23. The process of claim 14 or 15 wherein the polar solvent is selected from the group consisting of N-
5 methylpyrrolidone, N-methylformamide, N,N-dimethylformamide, N-methylacetamide, N,N-dimethylacetamide, tetramethylurea, dimethyl sulfoxide, and sulfolane.